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cyclo-Tetrakis(μ-oxo)tetrakis[iodo(η^5-methylcyclopentadienyl)titanium(IV)]

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Abstract

The title compound, $[Ti_4I_4O_4(C_6H_7)_4]$, displays the same geometric features as the analogous chloro complex; the central eight-membered (Ti–O)$_4$ ring deviates appreciably from planarity. The cyclopentadienyl and iodo ligands lie alternately above and below the ring. Approximate twofold symmetry is observed. The Ti—I and Ti—O bond lengths lie in the ranges 2.657 (4)–2.673 (4) and 1.763 (15)–1.845 (15) Å, respectively.

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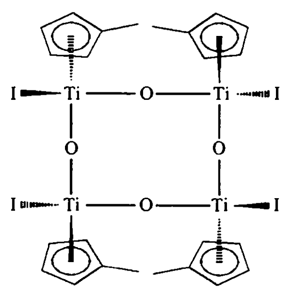
Comment

In the following discussion some comparable values for the known chloro(methylcyclopentadienyl) complex $[(MeC_5H_4)TiClO]_4$ (Petersen, 1980) are given in square brackets where applicable.

The 'backbone' of the title compound, (I) (Fig. 1), is formed by an eight-membered ring consisting of four O and four Ti atoms. The iodo and methylcyclopentadienyl ligands lie alternately above and below this ring.



(I)

In contrast to the corresponding chloro complex (Petersen, 1980), the iodo complex possesses no crystallographic C_2 symmetry along either of the vectors O2···O4 or O1···O3, or perpendicular to the ring. Nevertheless, there is an approximate twofold axis along the vector O2···O4. If the methyl groups are ignored (C26 and C36 point into the ring, and C16 and C46 point away from it), the approximate symmetry increases to 222.

In both complexes, the eight-membered ring deviates appreciably [mean deviation in (I) is 0.200 Å] from planarity. It is folded in (I) along the Ti1···Ti3 and Ti2···Ti4 axes giving two pairs of planes, *i. e.* Ti1–O1–Ti2–O2–Ti3 (mean deviation 0.065 Å) and Ti1–

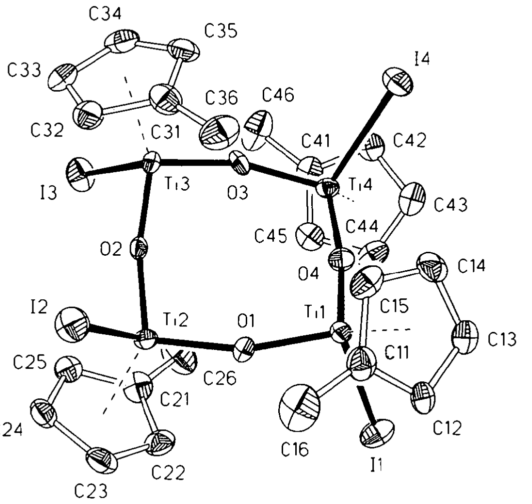


Fig. 1. The molecule of the title compound in the crystal. Radii are arbitrary. Displacement ellipsoids are plotted at the 50% probability level.

O4–Ti4–O3–Ti3 (mean deviation 0.018 Å), with an interplanar angle of 24.16 (10)°, and Ti2–O2–Ti3–O3–Ti4 (mean deviation 0.053 Å) and Ti2–O1–Ti1–O4–Ti4 (mean deviation 0.029 Å), with an interplanar angle of 24.38 (10)°. The corresponding interplanar angle in the chloro complex (Petersen, 1980) is 26°. The transannular Ti···Ti distances are Ti1···Ti3 4.984 (5) and Ti2···Ti4 4.991 (5) Å [4.964 Å].

The Ti—O—Ti angles lie in the range 155.9 (9) to 171.0 (9)° [157.2 (2) to 169.1 (2)°] with similar values for opposite O atoms. Angles of *ca* 170° have also been observed in many other oxo-bridged titanium complexes (Rausch, Sikora, Hrncir, Hunter & Atwood, 1980; Thewalt & Klein, 1981; Shur *et al.*, 1983; Honold *et al.*, 1986).

The coordination geometry at the Ti atoms is distorted tetrahedral (regarding the centres of gravity *X*1*A*–*X*1*D* of the methylcyclopentadienyl rings C11–C15, *etc.* as monodentate ligands), with angles ranging from 99.5 (5) to 119.1° [101.6 (1) to 118.9 (3)°]. The O—Ti—O angles lie in the range from 104.7 (6) to 105.2 (6)°.

The Ti—O bond lengths, 1.763 (15) to 1.845 (15) Å, [1.792 (3) to 1.801 (3) Å], lie in the expected range, which is also found in many other oxo-bridged titanium complexes (Skapski & Troughton, 1970; Rausch *et al.*, 1980; Thewalt & Klein, 1981; Shur *et al.*, 1983; Honold *et al.*, 1986; Thewalt & Schomburg, 1977; Thewalt & Schleussner, 1978; Thewalt & Kebbel, 1978; Le Page, McCowan, Hunter & Heyding, 1980; Klein, Thewalt, Döppert & Sanchez-Delgado, 1982; Bottomley, Egharevba, Lin & White, 1985; Iiskola *et al.*, 1993).

The distances between the Ti atoms and the centres *X* of the MeCp rings lie in the range from 2.018 to 2.041 Å [2.034 to 2.040 Å], which is typical for oxo-bridged titanium complexes with only one cyclopentadienyl ligand, as the following values indicate: 2.010 Å in $[\mathrm{CpTiCl_2}]_2\mathrm{O}$ (Thewalt & Schomburg, 1977), 2.02 and 2.04 Å in $[\mathrm{CpTiClO}]_4$ (Skapski & Troughton, 1970). This is somewhat shorter than the distance in comparable complexes with two cyclopentadienyl ligands, with an average value of 2.078 Å (Rausch *et al.*, 1980; Thewalt & Klein, 1981; Shur *et al.*, 1983; Honold *et al.*, 1986; Thewalt & Schleussner, 1978; Thewalt & Kebbel, 1978; Le Page *et al.*, 1980; Klein *et al.*, 1982). The vertical distances of the Ti atoms to the planes of the MeCp rings are 2.029 (10), 2.029 (10), 2.018 (10) and 2.040 (10) Å for Ti1–Ti4, respectively.

Reported values for Ti—I bond lengths are scarce, but the values from 2.657 (4) to 2.673 (4) Å in (I) are comparable with those in $[\mathrm{Ti(OAr)_3I}]$ (OAr is 2,6-di-*tert*-butylphenol) with 2.634 (8) Å (Latesky, Keddington, McMullen, Rothwell & Huffman, 1985).

Experimental

The title compound was obtained unexpectedly from the following reaction sequence: a solution of $[(\mathrm{MeCp})_2\mathrm{TiCl_2}]$ in THF was treated sequentially with lithium triethylborohydride, powdered grey selenium and methyl iodide. Removal of the solvent, extraction of the resulting black slurry with dichloromethane, filtration, renewed removal of the solvent and addition of acetone gave the product as a yellow powder. Crystals were grown by evaporation from dichloromethane.

Crystal data

$[\mathrm{Ti_4I_4O_4(C_6H_7)_4}]$
$M_r = 1079.66$
Orthorhombic
$Pna2_1$
$a = 19.239(3)$ Å
$b = 10.500(2)$ Å
$c = 15.696(2)$ Å
$V = 3170.7(9)$ Å^3
$Z = 4$
$D_x = 2.262$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 54 reflections
$\theta = 10.0$–$11.5°$
$\mu = 4.893$ mm^{-1}
$T = 143(2)$ K
Plate
0.50 × 0.25 × 0.05 mm
Yellow

Data collection

Stoe Stadi-4 diffractometer
ω–θ scans
Absorption correction: ΔF (*SHELXA*; Sheldrick, 1993*a*)
$T_{\min} = 0.447$, $T_{\max} = 0.699$
5730 measured reflections
5449 independent reflections
3776 reflections with $I > 2\sigma(I)$

$R_{\mathrm{int}} = 0.0616$
$\theta_{\max} = 25.03°$
$h = 0 \rightarrow 22$
$k = -12 \rightarrow 1$
$l = -18 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 2.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0766$
$wR(F^2) = 0.1860$
$S = 1.018$
5449 reflections
330 parameters
H atoms: methyl H atoms rigid, others riding
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 52.2807P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.002$
$\Delta\rho_{\max} = 1.216$ e Å^{-3}
$\Delta\rho_{\min} = -1.071$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.65 (9)

Table 1. *Selected geometric parameters (Å, °)*

I1—Ti1	2.673 (4)	Ti3—O3	1.808 (13)
Ti1—O4	1.763 (15)	O3—Ti4	1.801 (14)
Ti1—O1	1.807 (15)	Ti4—O4	1.845 (15)
O1—Ti2	1.820 (14)	Ti4—I4	2.670 (4)
Ti2—O2	1.826 (15)	*X*1*A*—Ti1	2.031
Ti2—I2	2.669 (4)	*X*1*B*—Ti2	2.031
I3—Ti3	2.657 (4)	*X*1*C*—Ti3	2.018
Ti3—O2	1.795 (15)	*X*1*D*—Ti4	2.041
O4—Ti1—O1	105.1 (6)	Ti4—O3—Ti3	156.3 (8)
O4—Ti1—I1	99.5 (5)	Ti1—O4—Ti4	171.0 (9)
O1—Ti1—I1	104.2 (5)	*X*1*A*—Ti1—O1	114.3
O1—Ti2—O2	104.7 (6)	*X*1*A*—Ti1—O4	118.6
O1—Ti2—I2	103.7 (5)	*X*1*A*—Ti1—I1	113.3
O2—Ti2—I2	100.5 (4)	*X*1*B*—Ti2—O1	116.8
O2—Ti3—O3	105.2 (6)	*X*1*B*—Ti2—O2	114.3
O2—Ti3—I3	101.9 (5)	*X*1*B*—Ti2—I2	115.0
O3—Ti3—I3	103.6 (5)	*X*1*C*—Ti3—O2	114.3
O3—Ti4—O4	104.8 (6)	*X*1*C*—Ti3—O3	115.0
O3—Ti4—I4	102.1 (5)	*X*1*C*—Ti3—I3	115.4

O4—Ti4—I4	99.7 (5)	*X*1*D*—Ti4—O3	114.6
Ti1—O1—Ti2	155.9 (9)	*X*1*D*—Ti4—O4	119.1
Ti3—O2—Ti2	168.2 (7)	*X*1*D*—Ti4—I4	114.2

An attempt was made to perform an absorption correction based on ψ scans, but the weak diffraction caused too few suitable reflections to be available. Accordingly, recourse to a ΔF correction had to be made. The transmission factors are somewhat higher than expected. The number of least-squares parameters was artificially increased by 18 to allow for the extra (hidden) parameters introduced. The structure was refined as a racemic twin with components 0.67, 0.33 (11); the origin was fixed by the method of Flack & Schwarzenbach (1988). The high *R* values are associated with broad reflection profiles, weak diffraction from a thin plate and (probably) residual absorption errors. To improve the refinement stability, a system of restraints (695 in all) to light-atom temperature-factor components and local Cp-ring symmetry was employed.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993*b*). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1201). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. LXXXIII. Heptaaquacalcium 1,2-Benzenedisulfonimide†

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Abstract

In heptaaquacalcium bis[1,3,2-benzodithiazole 1,1,3,3-tetroxide(1−)], $[Ca(H_2O)_7](C_6H_4NO_4S_2)_2$, the calcium ion is surrounded by the O atoms of seven water molecules in a distorted pentagonal bipyramidal geometry. The structure displays layers of anions, with the calcium cations and water molecules between these layers. The layers are held together by an extensive network of hydrogen bonds involving the water molecules and the $(SO_2)_2N^-$ subunits of the anions.

Comment

Calcium ions in crystal structures generally bind to O atoms in ligands and their preferred coordination numbers range from 6 to 8 (Katz, Glusker, Beebe & Bock, 1996). However, in hydrated compounds containing six or more water molecules per calcium ion, exclusive hydration of the metal to form $[Ca(H_2O)_n]^{2+}$ ($n \geq 6$) is rare; in most of these compounds, the coordination polyhedra involve ligands other than water molecules. It was shown by *ab initio* molecular orbital calculations *in vacuo* that the net energy penalty for changing the number of water molecules in the first coordination shell of Ca^{2+} between 6 and 8 is extremely small (Katz *et al.*, 1996).

The heptahydrated calcium ion has been observed in $CaCr_2O_7.2[(CH_2)_6N_4].7H_2O$ (Dahan, 1975),

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† Part LXXXII: Dalluhn, Henschel, Blaschette & Jones (1997).

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